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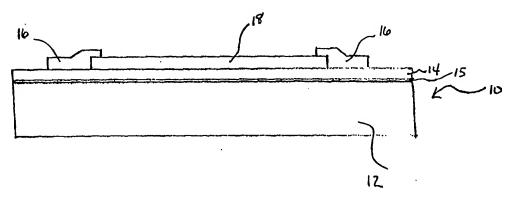
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(54) Title: RESISTORS WITH LOW TEMPERATURE COEFFICIENT OF RESISTANCE AND METHODS OF MAKING



(57) Abstract

The present invention relates to a method of making a resistor having a low temperature coefficient of resistance which includes applying a first resistor layer (18) and applying a second resistor layer over the first resistor layer (18), where either the first resistor layer (18) or the second resistor layer includes a diamond-like material. The diamond-like material includes carbon, hydrogen, and a metal, and has a low temperature coefficient of resistance. The present invention also relates to a resistor.





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# RESISTORS WITH LOW TEMPERATURE COEFFICIENT OF RESISTANCE AND METHODS OF MAKING

#### FIELD OF THE INVENTION

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The present invention relates generally to resistors with low temperature coefficient of resistance and a method of making the resistors.

#### **BACKGROUND OF THE INVENTION**

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As is well known, integrated circuits and thin film devices frequently require resistors as part of the circuitry, and film resistors are commonly used. Thin film resistors generally consist of a thin film of resistive material deposited, for example, by sputter deposition, on a layer or substrate of insulative material with end contracts on the resistive material. The end contracts or interconnections are then connected to circuit components in a conventional manner.

The resistors are expected to have a well characterized temperature dependence for device design and operation. It is desired that the temperature dependence be as small as possible. The temperature dependence of resistance is called the temperature coefficient of resistance ("TCR"). Thus, the lower the TCR, the better the resistor.

Commercially available thin film resistors are mainly fabricated with intrinsic and doped poly-silicon, semi-insulating polycrystalline silicon having a conductivity degrading impurity such as oxygen or nitrogen (U. S. Patent Number 5,712,534), tantalum nitride (TaN), nichrome (NiCr), titanium oxynitride, or tantalum oxynitride as the resistive material. However, such materials have significant deficiencies, such as limited range of electrical tailorability, high TCR, and/or limited stability.

Typically, the TCR varies linearly with the resistance value and, thus, the higher the resistance, the higher the TCR. Thus, making resistors having a high resistance value with low TCR is extremely challenging.

The present invention is directed toward overcoming these deficiencies.

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#### SUMMARY OF THE INVENTION

One aspect of the present invention relates to a resistor having a low temperature coefficient of resistance. The resistor includes a layer of conductive material and a layer of resistive material in contact with the layer of conductive material, where the layer of resistive material includes a diamond-like material including C, H, and a metal, where the diamond-like material has a low temperature coefficient of resistance.

Another aspect of the present invention relates to a method of making a resistor having a low temperature coefficient of resistance. The method includes applying a first resistor layer over a substrate and applying a second resistor layer over the first resistor layer, where one of the first resistor layer or the second resistor layer is a diamond-like material comprising C, H, and a metal, and where the diamond-like material has a low temperature coefficient of resistance.

The resistors of the present invention utilize a material which has a low temperature coefficient of resistance ("TCR"), thus, the resistors have a low TCR. In addition, the material used in the present invention is extremely hard, wear resistant, long lasting, impervious, and thermally stable. Further, the materials can be deposited on a variety of substrate materials.

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#### DETAILED DESCRIPTION OF THE DRAWINGS

Figures 1A and 1B illustrate schematic side views of two embodiments of resistors of the present invention.

Figure 2 illustrates a flow chart of one embodiment of a method of the present invention.

Figure 3 illustrates a flow chart of a second embodiment of a method of the present invention.

Figure 4 illustrates an apparatus for depositing the diamond-like material of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

One aspect of the present invention relates to a resistor having a low temperature coefficient of resistance. The resistor includes a layer of conductive material and a layer of resistive material in contact with the layer of conductive material, where the layer of resistive material includes a diamond-like material which



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includes C, H, and a metal, where the diamond-like material has a low temperature coefficient of resistance.

Figures 1A and 1B illustrate sectional side views of two embodiments of resistors 10 of the present invention. As shown in Figure 1A, resistor 10 includes a substrate 12 having a conductive layer 16 and a resistor layer 18 overlying conductive layer 16. Alternatively, as shown in Figure 1B, resistor 10 has resistor layer 18 underlying conductive layer 16. As shown in both Figures 1A-B, conductive layer 16 is in contact with, and partially overlaps, resistor layer 18. In both embodiments, typically, conductive layer 16 is made of a plurality of patterned shapes as end contacts, such as pads, which protrude from an upper surface of substrate 12, as shown in Figures 1A and 1B. The dimensions of these patterned shapes and the dimensions between the patterned shapes can be calculated by those of ordinary skill in the art.

Substrate 12 is formed of any suitable material known to one of ordinary skill in the art, such as dielectric materials and films, such as Kapton®(DuPont, Wilmington, DE), Upilex®, (Ube Industries, Japan)

Ultem®(General Electric Co., Pittsfield, MA) silicon, silicon oxide, glass, quartz, alumina, aluminum, aluminum nitride, germanium, and gallium arsenide. Optionally, substrate 12, where desired, has a dielectric layer 14 overlying substrate 12. Dielectric layer 14 preferably includes a polymer film having a low coefficient of thermal expansion ("CTE") and includes such films as Kapton®, or other polymers, or layers such as SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, or undoped diamond-like nanocomposite ("DLN") films as described in U.S. Patent No. 5,466,431 to Dorfman et al., which is hereby incorporated by reference. Dielectric layer 14 is adhered to substrate 12 by methods known to those of ordinary skill in the art, such as lamination using an adhesive material 15.

Optionally, substrate 12 is itself a dielectric material and, thus, no dielectric layer 14 is required. Resistors are generally described in U.S. Patent No. 5,683,928 to Wojnarowski et. al., which is hereby incorporated by reference.

The material used as the resistor material in the resistive layer in the present invention is a diamond-like carbon and silicon-containing coating having a low TCR. As used herein, "diamond-like" refers to a material having many of the technologically important properties of diamond, such as high hardness, high chemical stability, electrochemical and wear resistance, high electrical resistivity, and high thermal conductivity. As used herein, "temperature coefficient of resistance" relates to the variance of the sheet resistance of the resistor with temperature. A low temperature coefficient of resistance is defined herein as a TCR of between about -1.0%/°C to about 1.0%/°C. Particularly preferred is a TCR of from about -0.006%/°C to about -1.0%/°C.

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The preferred materials comprise a two component structure which includes a diamond-like C-H network with one or more metal networks. Typically, the metal in the metal networks is selected from Group 1-7b of the periodic table of elements. Particularly preferred are metals from groups, IB, IVB, or VIB of the periodic table of elements. Preferably, the material of the present invention is a three component structure which includes the C-H network, the one or more metal networks, and a Si-O network. Further, additional metals and non-metals may be incorporated as an optionally present dopant network. The networks are bonded to one another mainly by weak chemical bonds.

One particularly preferred material comprises a carbon network chemically stabilized by hydrogen atoms, and a silicon network stabilized by oxygen atoms resulting in an amorphous structure. "Amorphous " as used herein refers to a random structure or arrangement of atoms in a solid state that results in no long range regular ordering, and no crystallinity or granularity. Such materials have an amorphous structure and do not contain ordered clusters greater than about ten Angstroms. This absence of clusters at the atomic scale is a characteristic of these preferred coatings used in connection with the present invention.

Depending upon the required electrical resistivity in a particular application, the material may have one or more separate disordered networks of dopant designed to tailor or tune the resistance. The dopant may be any one or a combination of the transition metals and non-metals of the Groups 1-7b and 8 of the periodic table. Further, silicon and oxygen atoms may also be used in the dopant networks with other elements and compounds.

Preferred dopant elements to be used in the coating are B, Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Mn, Ni, Zr, Cr, Re, Hf, Cu, Al, N, Ag and Au. Particularly preferred dopants include Ti, W, Zr, Cr, Hf, Cu, Al, Ag, and Au, with Ti and W being highly preferred.

The carbon content in the preferred diamond-like material of the present invention is greater than about 40 atomic % of the coating, preferably from about 40 to about 98 atomic %, more preferably from about 50 to about 85 atomic %. Although such coatings may theoretically be prepared without any hydrogen, the hydrogen content is preferably at least about 1 atomic % up to about 40 atomic % of the carbon concentration. The metal content is greater than or equal to about 5 atomic % of the coating. The sum of the silicon, oxygen and dopant, if present, is greater than about 2 atomic % of the diamond-like material composition. In one preferred embodiment, the ratio of carbon to silicon atoms is from about 4:1 to about 9:1, carbon to hydrogen atoms is from about 1.1:1 to about 2.5:1, silicon to oxygen atoms

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is about 0.6:1 to about 1.7:1, and dopant to carbon atoms is about 0.06:1 to about 1.5:1. The density of the C-H and Si-O two network coating varies from about 1.8 to about 2.1 g/cm<sup>3</sup>.

The preferred coatings of the present invention are diamond-like carbon-containing coatings synthesized via a glow discharge plasma process as would be readily understood by one skilled in the field of thin film deposition. Carbon-containing radicals can be produced by plasma discharge and deposited on a substrate applied with a high-voltage field in a vacuum chamber. The composition of the coatings of the present invention include but are not limited to the coatings that are the subject of U.S. Patent No. 5,466,431 to Dorfman et al., which is hereby incorporated by reference.

The conductive layer of the present invention is a conductive material formed of a metal. Preferred metals include aluminum, silver, titanium, chromium, gold. tungsten, tantalum, and molybdenum.

Another aspect of the present invention relates to a method of making a resistor having a low temperature coefficient of resistance. The method includes applying a first resistor layer over a substrate and applying a second resistor layer over the first resistor layer, where one of the first resistor layer or the second resistor layer is a diamond-like material comprising C, H, and a metal, and where the diamond-like material has a low temperature coefficient of resistance.

One example of a method of fabricating resistors with low TCR is depicted in Figure 2. A first shadow mask 20 for first resistor layer 16 is made with a desired pattern. First shadow mask 20 is made of a material known to those of ordinary skill in the art, such as stainless steel. First shadow mask 20 for first resistor layer 16 is positioned over a substrate 12 as shown in Figure 2A. Optionally, as discussed above, if desired, a dielectric layer 14 is adhered to substrate 12 prior to deposition of first resistor layer 19. The first resistor layer material M<sub>1</sub> is deposited by evaporation or magnetron sputtering through first shadow mask 20 so that first resistor layer 16 is deposited on substrate 12 in the pattern as show in Figure 2B. Typically, this layer is a metal layer and, typically, the pattern formed is of two metal pads which are separated by a known distance, as shown in Figure 2B. Following the deposition of first resistor layer material M<sub>1</sub>, a second shadow mask 22 with the desired pattern for second resistor layer 18 is positioned over the substrate 12. Second shadow mask 22 is positioned such that there will be a partial overlap between second resistor layer 18 to be deposited and the underlying first resistor layer 16, as shown in Figure 2C. Next, second resistor layer material M<sub>2</sub> is deposited through second shadow mask 22 to result in the pattern for second resistor layer 18 as



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shown in Figure 2D, thereby producing resistor 10. Second resistor layer material M<sub>2</sub> is the diamond-like material described above.

A second example of fabricating the resistors of the present invention is illustrated in Figures 3A-G. In this method, the second resistor layer material of the present invention is reactive ion etched to form resistors which are small and more intricate. Reactive ion etching is performed using the methods known to those of ordinary skill in the art. In particular, a blanket deposition of a second layer of resistive material which is the diamond-like resistive material of the present invention is made over the surface of substrate 12 to produce substrate 12 having a diamondlike material layer 18, as shown in Figure 3A. Next, a first photoresist layer 34 is formed by depositing photoresist material P, over diamond-like material layer 18 and patterning first photoresist layer 34 to the desired shape, using conventional photolithography known to those of ordinary skill in the art. The resulting structure is as shown in Figure 3B. Next, substrate 12 having diamond-like material layer 32 and first photoresist layer 34 is loaded into a reactive ion etch system as known by those of ordinary skill in the art. The exposed diamond-like material layer 32 is etched with an etching gas, such as CF<sub>4</sub>, CHF<sub>3</sub>, and/or oxygen gas. First photoresist layer 34 is then stripped by methods known by those of ordinary skill in the art to produce a patterned resistor 36, as shown in Figure 3D. Next, a second photoresist layer 38 is formed by depositing a second photoresist material P2 and patterning second photoresist material P<sub>2</sub> to the desired shape, as shown in Figure 3E. Following this step, a metal M3 (where the metals are, for example, chromium, titanium, tungsten) is deposited by evaporation or magnetron sputtering over second photoresist layer 38 on to substrate 12, as shown in Figure 3G to produce a first resistor layer 16 having the desired shape. Following the metal deposition, second photoresist layer 38 is stripped by methods known to those of ordinary skill in the art to yield a multi-layered resistor structure 10, as shown in Figure 3G, which includes substrate 12, first resistor layer 16, and second resistor layer 18. As known by those of ordinary skill in the art, a number of resistor structures can be created on a single substrate by creating multiple resistor and metal patterns during each of the above-identified photoresist patterning steps. Reactive ion etching of the material of the present invention can be performed selectively with good etching rates (500Å/min) using chemistries known to those of ordinary skill in the art. Excellent resolution can also be obtained with these reactive ion etch chemistries.

Figure 4 shows one preferred embodiment of the coating chamber used for depositing the preferred diamond-like carbon-containing coatings. A vacuum deposition chamber 100 is provided to coat a substrate sample 150. A precursor inlet



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system, comprises a metal tube 112 and a diffuser head 120 through which a liquid precursor, preferably a polysiloxane, is injected. The precursor inlet system is shown incorporated into the chamber 100 through the chamber back plate 130. The samples are loaded into the chamber through a load lock. The chamber comprises a resistively heated tungsten filament 140. Substrates 150 to be coated are attached to the substrate holder 160. The power supply 180 is used for biasing the substrates (DC or RF). In addition, a power supply (not shown) is used to bias the filament 140 and a power supply (not shown) is used to power magnetron 190. In practice, the system is "pumped down" using normal vacuum pumpdown procedures. Gate valves located in port 170 are closed and the system is backfilled with dry air, nitrogen or argon until the chamber reaches atmospheric pressure. The chamber is then opened and substrates 150 to be coated are attached to the substrate holder 160 using any fixtures or fastening means including clips, screws, clamps, etc. Magnetron 190 is used for codeposition of metals and other dopants.

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The precursor can also be introduced into the deposition chamber by liquid-to-vapor delivery system. The liquid-to-vapor delivery system is a conventional off-the-shelf component known in the field of vacuum technology. The precursor is stored in a reservoir and is delivered to a flash evaporator. The precursor is flash evaporated into a vapor. A mass flow controller is used to precisely control the flow rate of the precursor vapor. While not required, a mixing gas, such as argon, methane, acetylene, toluene can be used to assist precursor evaporation.

The high vacuum is achieved by roughing down the chamber with a mechanical pump followed by pumping with a high vacuum pump. The pump can be a diffusion pump, turbomolecular pump, cryogenic pump, or other high vacuum pumps known in the field of vacuum technology. The coatings required according to the process of the present invention can be carried out in a batch type process for small volumes. In such instance, substrates 150 are mounted on substrate holder 160 inside the deposition chamber, the chamber is evacuated, the deposition is performed, and the chamber is vented, followed by removal of the coated parts (substrates).

For larger volumes, the process of the present invention can be carried out in an cluster tool. The cluster tool concept is one which is known in the field of semiconductor technology. After cleaning of the substrates, the substrates are loaded in a cartridge capable of carrying many substrates at a time, use of mechanized/robotic loading of the substrates into the chamber. The substrates are loaded into a load-lock chamber, followed by entry into a pre-cleaning module, into the deposition chamber, and coating. After coating the substrates can then be removed from the deposition chamber into a load-lock chamber, followed by exit into the atmosphere onto a



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cartridge carrier. It is understood that the substrates to be coated may be rotated, tilted, or otherwise oriented, or manipulated while on the robotic arm, and at other instances during processing.

The substrates may have to be rotated, tilted and vibrated during mounting on the substrate holder. Vertical orientation is preferred to minimize particulate or debris accumulation and contamination of substrate surfaces. The deposition chambers are evacuated with low turbulence vacuum pumping to minimize particulate and debris being deposited on the substrate surfaces.

The chambers are evacuated to a base pressure below 10<sup>-5</sup> Torr after loading the substrates. Argon gas is then introduced into the chamber to raise the chamber pressure to 10<sup>-3</sup> to 10<sup>-4</sup> Torr. The substrates are then argon ion cleaned inside the deposition chamber before coating.

The argon ion cleaning is accomplished by either of two methods: glow discharge cleaning or hot filament assisted plasma cleaning. In glow discharge cleaning, the argon gas is introduced until the chamber pressure is in the 10<sup>-3</sup> Torr range. A glow discharge is excited by RF or DC. During the discharge, a substrate bias of from about 0.03 to about 5.0kV can be used. The frequency of the RF is in the range of 90-450 kHz. For plasma cleaning, the argon ions are created by a hot filament discharge and the chamber pressure is in the 10- Torr range. The temperature of the filament is in the range of from about 2100° to about 2950°C, with a DC filament bias of from about 70 to about 150 V. The substrates are biased by either RF or DC, as mentioned above. Other ion sources known in the field of deposition coating such as, Kaufmann type ion sources, RF coil, RF parallel plate etc. can also be used for ion generation. In addition to argon ion etching, other plasma cleaning can be performed by the introduction of small amounts of reactive gases such as oxygen gas with argon gas. The ion cleaning process has been found to efficiently remove hydrocarbon contamination, and other contaminants, as well as improve the adhesion of coatings deposited on substrates.

Towards the end of the substrate cleaning, organosilicon precursors, preferably siloxanes which contain C, H, Si, and O are introduced into the chamber. These precursors preferably have 1 to 10 silicon atoms. The preferred precursor is a polyphenylmethylsiloxane, with 2-3-4 triphenyl-nonamethyl-pentasiloxane being particularly preferred. The precursor is introduced directly into the active plasma region using a microporous ceramic or metallic dispenser which is heated by the hot filament. The precursor can be mixed with other gases, both inert (argon as the feed gas) and active gases such as hydrogen, methane, acetylene, butane, toluene etc. The hot filament photon and electron emission causes fragmentation and ionization of the

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precursor. The precursor can also be introduced into the system using liquid-to-vapor delivery systems consisting of flow controller, a heater, and a dispenser as known in the field. In the case of liquid delivery systems, the ionization source can be a hot filament isolated from the precursor delivery system or a Kaufmann ion source or a RF parallel plate.

Metal-containing species can be incorporated into the growing films and coatings by many methods: (a) thermal evaporation; (b) magnetron sputtering; (c) ion beams, (d) organometallic CVD etc. The metal beams are directed toward the substrate by the appropriate placement of the sources.

Variations of the above described deposition process include: (a) the use of sputtered silicon and oxygen gas as sources for Si and O; (b) use of solid SiO2 as a source for Si and O; (c) use of SiH4 and oxygen-containing gases as sources for Si; (d) use of a graphite target, hydrogen, and hydrocarbon gases as sources of C and H; (e) use of metal-containing organosilicon compounds as sources of C, H, Si, O and metal; and (f) use of metallo-organic compounds as a source of metal in conjunction with organosilicon compounds as a source of C, H, Si and O. Combination of the aforementioned methods may be used.

The coating deposition preferably is sustained by a RF capacitively coupled discharge (CCD). The organosilicon and organometallic precursors can be introduced by either a separately heated microporous ceramic or metallic dispenser, or one of the liquid vapor injection systems described previously. The precursor can be mixed with other gases, both inert with argon as the feed gas, or active gases such as hydrogen, methane, acetylene, butane, toluene, etc., to achieve deposition pressures typically in the 10-2 Torr range. A single plate or parallel plate configuration can be used. The substrates are attached to one of the plates. RF or PDC voltage is then applied. In the case of a capacitive RF discharge, the frequency of the RF is in the range of 100 kHz to 100Mhz. In another method, a large RF antenna can be placed inside the chamber to excite the discharge. The antenna can be made of copper, stainless steel, or other known state of the art materials. A protective coating, such as porcelain, can be applied to the surface of the antenna to prevent sputtering.

A DC of RF potential is generally applied to the substrates during the deposition process. No external substrate heating is required, but heating may be used if desired. The substrate holder may be designed specifically to hold parts of different shapes such as cylinders, as would be readily apparent to one skilled in the field.

The deposition may be "tuned" to meet the sheet resistance required for a particular application. This may be done by altering the composition of the metal in the diamond-like material. Further, the ability to tailor the amount of metal

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in the diamond-like coatings makes it possible to compatibly coat a variety of microelectronic substrate materials such as Kapton<sup>®</sup>, silicon, silicon oxide, glass, alumina, aluminum nitride, germanium, and gallium arsenide. It is believed that this "tunability" contributes to the coatings' resistivity tailorability.

In addition to resistivity tailorability, the coatings exhibit very low temperature coefficient of resistance. Known resistors made from polysilicon and TaN are limited in the above aspects, by comparison, as shown in the examples below. The resistors of the present invention made with the carbon, silicon and metal-containing coating disclosed above have resistivity values (depending upon the dopant selected, dopant concentration, etc.) in the range of from about 0.2 Kohms/square to about 15 Mohms/square. Further, utilizing the method of the present invention, the resistors have a resistance uniformity of 5 to 10%.

The improved resistivity tailorability and the low TCR characteristics of the present invention make these coatings many times superior than known materials in the field of microelectronics.

The resistors can be stabilized by annealing in a non-oxidizing environment. The resistors can be heated in a vacuum or inert environment to approximately 175° to 250°C for 20 to 30 minutes. This allows the resistor value to stabilize. The annealing step can be performed in-situ after the deposition or in a annealing furnace with a controlled atmosphere.

The resistors of the present invention display excellent thermal stability, operating at temperatures as high as 200°C in air and 400°C in an inert atmosphere, with the resistors showing no degradation in resistivity and TCR properties.

Since the resistor is deposited in a low temperature process, the deposition process does not affect or damage other layers in a microelectronic device.

The resistor has very good thermal stability and is stable in air up to 500° C and up to 800° C in a non-oxidizing atmosphere. Because of this thermal stability, post processing of a microelectronic device with the resistors of the present invention at temperatures as high as 350° to 450° C is possible.

The resistors are deposited in a alkali-free environment, hence problems of mobile interface states are mitigated. Thus, the deposition process and the resistors produced are compatible with a semiconductor fabrication process.

The following examples serve only to further illustrate aspects of the present invention and should not be construed as limiting the invention.

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#### **EXAMPLES**

# Example 1 - Deposition of a Titanium-doped Resistive Pattern over a Silver Conductive Layer

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Five alumina substrates with a screen printed conductive pattern of silver were ultrasonically cleaned in acetone, methylene chloride, and methanol, dried with nitrogen gas and mounted on a 24" substrate holder. Control samples of silicon, glass, carbon steel, stainless steel, and bare alumina substrates were also cleaned in a similar fashion and mounted on the substrate holder. A shadow mask with the desired resistor pattern was placed over the alumina samples. A titanium target was mounted on the magnetron. The chamber was evacuated to a ultimate pressure of 8 x 10<sup>-5</sup> torr. Argon gas was introduced in to the chamber to raise the pressure to 10<sup>-2</sup> torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 400V. The substrates were argon ion-etched for 15 minutes at the above conditions. After 15 minutes of cleaning, the pressure was lowered to 4 x 10<sup>-4</sup> torr. The triode plasmatron was ramped up to generate a plasma current of 1.0A. The 2,3,4-triphenyl-nonamethyl-pentasiloxane precursor was introduced directly into the plasma and the magnetron was ramped up to 375 watts. The diamond-like coating deposition was performed under the above conditions for 90 minutes. This resulted in a 1.5 micron thick, highly adherent coating. The patterned resistor had an electrical resistance of 4.2 Kohms as measured using a conventional multimeter. The coating exhibited a hardness of 13.6 GPa as measured by nanoindentation using the continuous stiffness method described in U.S. Patent No. 4,848,141 to Oliver et al. which is hereby incorporated by reference.

### <u>Example 2</u> - <u>Deposition a Titanium-doped Resistive Pattern</u> <u>over a Chromium Conductive Layer</u>

Two smooth alumina substrates ( $R_a \sim 50\text{Å}$ ) were ultrasonically cleaned in acetone, methylene chloride and methanol, dried with nitrogen gas, and mounted on a 24" substrate holder. A shadow mask with the desired conductive pattern was placed over the alumina samples. A chromium target was mounted on the magnetron. The chamber was evacuated to a ultimate pressure of 8 x  $10^{-5}$  torr. Argon gas was introduced in to the chamber to raise the pressure to  $10^{-2}$  torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 400V. The substrates were argon ion-etch cleaned for 15 minutes at the above conditions. After 15 minutes of cleaning, the pressure was lowered to 4 x  $10^{-4}$  torr. The magnetron was ramped up to a power of 500 watts. A

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patterned layer of chromium was deposited under the above conditions for 30 minutes. Following the chromium deposition, the chamber was vented to the atmosphere. The chromium deposition resulted in a 0.5 micron thick chromium film. The shadow mask for the conductor pattern was removed. A second shadow mask with the desired resistor pattern was placed on the chromium coated alumina 5 substrates. Control samples of silicon, glass, carbon steel, stainless steel and bare alumina substrates that were ultrasonically cleaned in acetone, methylene chloride. methanol and dried in nitrogen gas were mounted on the substrate holder. The chromium target was removed and a titanium target was mounted on the magnetron. The chamber was evacuated to a ultimate pressure of 8 x 10<sup>-5</sup> torr. Argon gas was 10 introduced in to the chamber to raise the pressure to 10<sup>-2</sup> torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 800V. The substrates were argon ion-etched for 15 minutes at the above conditions. After 15 minutes of cleaning, the pressure was lowered to 4 x 10<sup>-4</sup> torr. The triode plasmatron was ramped up to generate a plasma current of 1.0A. 15 The 2,3,4-triphenyl-nonamethyl-pentasiloxane precursor was introduced directly into the plasma. The diamond-like coating deposition was performed under the above conditions for 90 minutes. This resulted in a highly adherent Ti-DLN coating of 1.5 micron thickness. The patterned resistor had an electrical resistance of 6.1 Kohms as measured using a conventional multimeter. 20

# <u>Example 3</u> - <u>Deposition of Tungston-doped Resistive Pattern</u> on Silicon Substrates

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A one inch square piece of silicon, one inch square piece of silicon with 5000Å thick silicon oxide, and one inch square glass substrate were ultrasonically cleaned in acetone, methylene chloride and methanol, dried with nitrogen gas and mounted on a 24" substrate holder. Control samples of silicon, glass, carbon steel and stainless steel were also cleaned in a similar fashion and mounted on the substrate holder. A shadow mask with the desired resistor pattern was placed over the one inch square of silicon and glass samples. A tungsten target was mounted on the magnetron. The chamber was evacuated to a ultimate pressure of 8 x 10<sup>-5</sup> torr. Argon gas was introduced in to the chamber to raise the pressure to 10<sup>-2</sup> torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 400V. The substrates were argon ion-etched for 15 minutes at the above conditions. After 15 minutes of cleaning the pressure was lowered to 4 x 10<sup>-4</sup> torr. The triode plasmatron was ramped up to generate a plasma current of 1.0A. The 2,3,4-triphenyl-nonamethyl-pentasiloxane

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precursor was introduced directly into the plasma and the magnetron was ramped up to 150 watts. The diamond-like coating deposition was performed along with tungsten metal deposition under the above conditions for 8 minutes. This resulted in a highly adherent W-DLN coating of 0.14 micron thickness. The patterned resistor on the glass substrate had a sheet resistance of 25.51 Kohms/square as measured using a multimeter. The film had a compressive stress of 667 MPa.

### Example 4 - Deposition of Titanium-doped Resistive Pattern on a 4 Inch Wafer

A four inch diameter of silicon with 5000Å thick silicon oxide and one inch square glass substrate were ultrasonically cleaned in acetone, methylene chloride and methanol, dried with nitrogen gas and mounted on a 24" substrate holder. Control samples of silicon, glass, carbon steel and stainless steel were also cleaned in a similar fashion and mounted on the substrate holder. A shadow mask with the desired resistor pattern was placed over the one inch piece of glass sample. A titanium target was mounted on the magnetron. The chamber was evacuated to a ultimate pressure of 8 x 10<sup>-5</sup> torr. Argon gas was introduced in to the chamber to raise the pressure to 10<sup>-2</sup> torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 400V. The substrates were argon ion-etched for 15 minutes at the above conditions. After 15 minutes of cleaning the pressure was lowered to 6.1 x 10<sup>-4</sup> torr. The triode plasmatron was ramped up to generate a plasma current of 1.0A. The 2,3,4-triphenylnonamethyl-pentasiloxane precursor was introduced directly into the plasma and the magnetron was ramped up to 485 watts. The diamond-like coating deposition was performed along with titanium metal deposition under the above conditions for 8 minutes. This resulted in a highly adherent Ti-DLN coating of 0.08 micron thickness. The resistor pattern on the oxidized silicon wafer had a sheet resistance of 2.7 Kohms/square as measured using a four probe system known in the state of the art of resistance measurement.

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## Example 5 - Deposition of Titanium-doped Resistive Pattern on 4 Inch Wafer

A four inch diameter of silicon with 5000Å thick silicon oxide and one inch square glass substrate were ultrasonically cleaned in acetone, methylene chloride and methanol, dried with nitrogen gas and mounted on a 24" substrate holder. Control samples of silicon, glass, carbon steel and stainless steel were also cleaned in a similar fashion and mounted on the substrate holder. A shadow mask with the desired resistor pattern was placed over the one inch piece of glass sample. A titanium target was mounted on the magnetron. The chamber was evacuated to a

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ultimate pressure of 8 x 10<sup>-5</sup> torr. Argon gas was introduced in to the chamber to raise the pressure to 10<sup>-2</sup> torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 409V. The substrates were argon ion-etched for 15 minutes at the above conditions. After 15 minutes of cleaning, the pressure was lowered to 4.6 x 10<sup>-4</sup> torr. The triode plasmatron was ramped up to generate a plasma current of 1.0A. The 2.3,4-triphenylnonamethyl-pentasiloxane precursor was introduced directly into the plasma and the magnetron was ramped up to 525 watts. The diamond-like coating deposition was performed along with titanium metal deposition under the above conditions for 8 minutes. This resulted in a highly adherent coating of 0.06 micron thickness. The resistive pattern on the oxidized silicon wafer had a sheet resistance of 1.4 Kohms/square as measured using a four probe system known in the state of the art of resistance measurement. The contact resistance of the coatings with Cu/Ti interconnect as measured by the transmission line method as known in the state of the art was 12 microohms/square centimeter. The TCR of the coating was -0.034%/°C.

#### Example 6 - Reactive Ion Etching of Resistive Layer

A one inch square piece of silicon with 0.06 micron thick diamondlike material layer was etched by reactive ion etching. Reactive ion etching was performed in a Samco RIE system (Sunnyvale, CA) at a pressure of 200 mTorr. The etching was performed with CF<sub>4</sub> gas at a flow rate of 30 sccm. Oxygen gas was added at a flow rate of 15 sccm. A power of 100W was used to etch the sample. The material etched with an etching rate of 580 Å/min. Uniform etching was observed with resolution down to 1.5 micron linewidth.

# Example 7 - Forming a Resistor Using Reactive Ion Etching and Photolithography

A one inch square piece of oxidized silicon and one inch square glass substrate were ultrasonically cleaned in acetone, methylene chloride and methanol, dried with nitrogen gas and mounted on a 24" substrate holder. Control samples of silicon, glass, carbon steel and stainless steel were also cleaned in a similar fashion and mounted on the substrate holder. A titanium target was mounted on the magnetron. The chamber was evacuated to a ultimate pressure of 8 x 10<sup>-5</sup> torr. Argon gas was introduced in to the chamber to raise the pressure to 10<sup>-2</sup> torr. The substrates were rotated at 7 revolutions per minute. An RF substrate bias was used and the substrate bias was ramped up to 409V. The substrates were argon ion-etched for 15 minutes at the above conditions. After 15 minutes of cleaning, the pressure was

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lowered to 4.6 x 10<sup>-4</sup> torr. The triode plasmatron was ramped up to generate a plasma current of 1.0A. The 2,3,4-triphenyl-nonamethyl-pentasiloxane precursor was introduced directly into the plasma and the magnetron was ramped up to 525 watts. The diamond-like coating deposition was performed along with titanium metal deposition under the above conditions for 8 minutes. This resulted in a highly adherent coating of 0.12 micron thickness. The diamond-like material was etched, into a resistor pattern, using reactive-ion etching and photolithography. The reactive ion etching was performed at 100W, with CF<sub>4</sub> at a flow rate of 30 sccm and a pressure of 200 mTorr and for a duration of 4 minutes. The resistive pattern on the oxidized silicon wafer had a sheet resistance of 1.4 Kohms/square as measured using a four probe system known in the state of the art of resistance measurement. The contact resistance of the coatings with Cu/Ti interconnect as measured by the transmission line method as known in the state of the art was 12 microohms/square centimeter. The TCR of the resistive pattern was -0.034%/°C.

Many other modifications and variations of the present invention are to the skilled practitioner in the field in light of the teachings herein. It is therefore understood that, within the scope of the claims, the present invention can be practiced other than as herein specifically described.



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#### What is Claimed:

- 1. A method of making a resistor having a low temperature coefficient of resistance comprising:
- applying a first resistor layer over a substrate and applying a second resistor layer over the first resistor layer, wherein one of the first resistor layer or the second resistor layer is a diamond-like material comprising C, H, and a metal, and wherein the diamond-like material has a low temperature coefficient of resistance.
- 10 2. The method according to claim 1, wherein the diamond-like material further comprises Si and O.
  - 3. The method according to claim 2, wherein the diamond-like material is formed of three networks, wherein the carbon is stabilized by hydrogen and the silicon is stabilized by oxygen.
- 15 4. The method according to claim 2, wherein the carbon, silicon, hydrogen and oxygen are obtained from the decomposition of an organosiloxane having from about 1 to about 10 silicon atoms.
  - 5. The method according to claim 4, wherein the organosiloxane is polyphenylmethylsiloxane.
- 20 6. The method according to claim 2, wherein the carbon content of the material is from about 40 atomic % to about 98 atomic %.
  - 7. The method according to claim 2, wherein the ratio of carbon to silicon is from about 4:1 to about 9:1.
- 8. The method according to claim 7, wherein the ratio of silicon to oxygen is from about 0.6:1 to about 1.7:1.
  - 9. The method according to claim 2, wherein the metal is selected from the Groups 1-7b of the periodic table.
  - 10. The method according to claim 9, wherein the metal is selected from Group IB, IVB, or VIB of the periodic table.

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The method according to claim 2, further comprising one or

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- more dopants selected from the group consisting of B, Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Ni, Ti, Zr, Cr. Re, Hf, Cu, Al, N, Ag, and Au.
- 12. The method according to claim 10, wherein the carbon content of the diamond-like material is at least 40 atomic % of the coating, the hydrogen content is up to about 40 atomic % of the carbon, the metal content is greater than about 5 atomic % of the diamond-like material, and the sum of the silicon, oxygen and dopants together is greater than about 2 atomic % of the coating.
- 13. The method according to claim 1, where the temperature coefficient of resistance is from about -0.006%/°C to about -1.0%/°C.
  - 14. The method according to claim 1, wherein the first resistor layer comprises a conductive material and the second resistor layer comprises a resistive material, wherein the resistive material is the diamond-like material.
- The method according to claim 14, wherein applying the first resistor layer comprises:

depositing a first resistor layer material by evaporation or sputtering and

applying the second resistor layer comprises depositing a second resistor layer material by co-deposition of particles.

- 20 16. The method according to claim 1, wherein the first resistor layer comprises a resistive material and the second resistor layer comprises a conductive material, wherein the resistive material is the diamond-like material.
  - 17. The method according to claim 16, wherein applying the first resistor layer comprises:
- etching a first resistor layer material with an etching gas and subjecting the etched first resistor layer to photolithography and
  - applying the second resistor layer comprises depositing a second resistor layer material using a photoresist layer and removing the photoresist layer.
- 30 18. A resistor having a low temperature coefficient of resistance comprising:

a layer of conductive material and

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a layer of resistive material in contact with the layer of conductive material, wherein the resistive material comprises a diamond-like material comprising C, H, and a metal, wherein the diamond-like material has a low temperature coefficient of resistance.

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- 19. The resistor according to claim 18, wherein the material further comprises Si and O.
- 20. The resistor according to claim 19, wherein the material is formed of three interpenetrating networks, wherein the carbon is stabilized by hydrogen and the silicon is stabilized by oxygen.
  - 21. The resistor according to claim 19, wherein the metal is selected from Groups 1-7b of the periodic table.

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- 22. The resistor according to claim 21, wherein the metal is selected from Groups IB, IVB, or VIB of the periodic table.
- 23. The resistor according to claim 21, further comprising one or more dopants selected from the group consisting of B, Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Ni, Ti, Zr, Cr, Re, Hf, Cu, Al, N, Ag, and Au.
  - 24. The resistor according to claim 19, wherein the carbon, silicon, hydrogen and oxygen are obtained from the decomposition of an organosiloxane having from about 1 to about 10 silicon atoms.
    - 25. The resistor according to claim 24, wherein the organosiloxane is polyphenylmethylsiloxane.
- The resistor according to claim 19, wherein the carbon content of the material is from about 40 atomic % to about 98 atomic %.
  - 27. The resistor according to claim 19, wherein the ratio of carbon to silicon is from about 4:1 to about 9:1.

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28. The resistor according to claim 19, wherein the ratio of silicon to oxygen is from about 0.6:1 to about 1.7:1.

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29. The resistor according to claim 23, wherein the carbon content of the diamond-like material is at least 40 atomic % of the coating, the hydrogen content is up to about 40 atomic % of the carbon, the metal content is greater than about 5 atomic % of the diamond-like material, and the sum of the silicon, oxygen and dopants together is greater than about 2 atomic % of the diamond-like material.

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30. The resistor according to claim 19, wherein the temperature coefficient of resistance is from about -0.006%/°C to about -1.0%/°C.

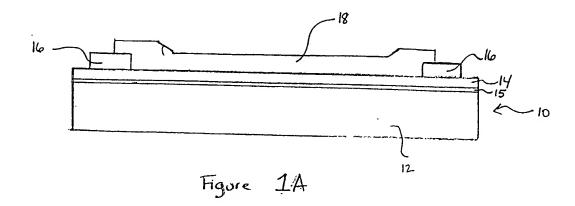
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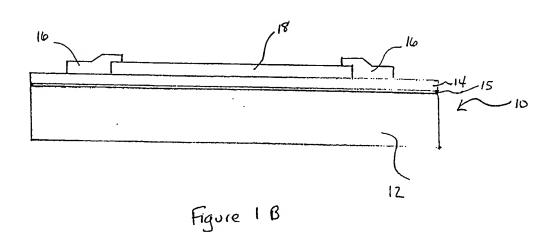
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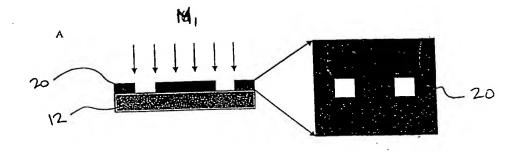


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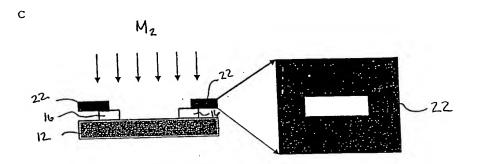






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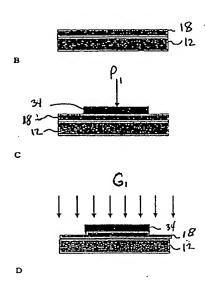
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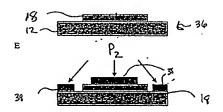


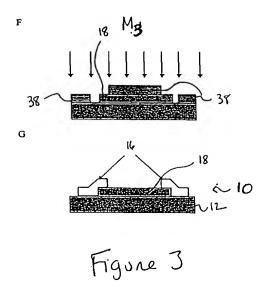
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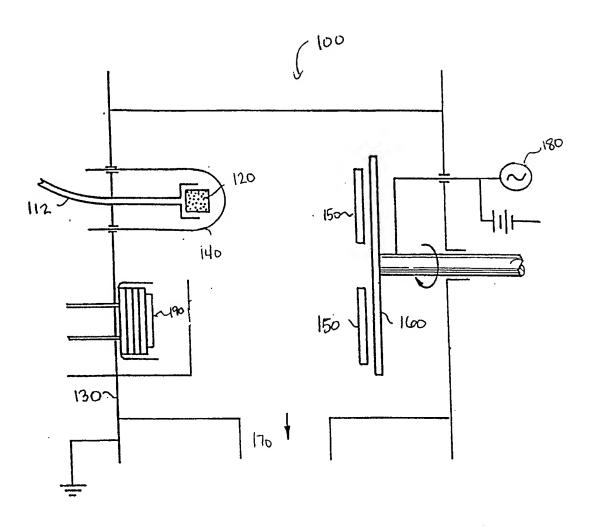


FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No. PCT/US99/10981

IPC(6) :HOIC 1/012 US CL :338/309 According to International Patent Classification (IPC) or to both national classification and IPC  3. FIELDS SEARCHED  Minimum documentation searched (classification system followed by classification symbols) U.S. : 338/309  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  NONE  C. DOCUMENTS CONSIDERED TO BE RELEVANT  Category*  Citation of document, with indication, where appropriate, of the relevant passages  Relevant to claim No.  1-30  US 5,352,493 A (DORFMAN et al) 04 October 1994, col. 6. lines 1-30  I-10.  Y. US 5,466,431 A (DORFMAN et al) 14 November 1995, col. 3, 1-30				<u></u>			
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C. DOCUMENTS CONSIDERED TO BE RELEVANT  Category* Citation of document, with indication, where appropriate, of the relevant passages  Relevant to claim No.  1-30  US 5,352,493 A (DORFMAN et al) 04 October 1994, col. 6. lines 1-10.  Y US 5,466,431 A (DORFMAN et al) 14 November 1995, col. 3, lines 50-68.  Y,P US 5,786,068 A (DORFMAN et al) 28 July 1998, col. 5, lines 35- 60.  See patent family annex.  **A* document defining the general state of the set which is not considered to be of particular relevance, the claim of invention cannot be called the document which may throw double on priority claim (a) or which claim of washing the guideline of the office of the actual to depth of the claim of the continuation of the international filing date observed to invention of the international filing date of the actual to depth of the claim of the continuation of the international filing date of the actual to depth of the claim of the continuation of the international filing date of the actual to depth of the claim of the international filing date of the actual to depth of the claim of the international filing date of the actual to depth of the claim of the international filing date of the actual to depth of the claim of the international filing date of the actual to depth of the international filing date of the actual to depth of the international filing date of the actual to depth of the international filing date to the considered of the claim of the international search  22 JUNE 1999  Name and mailing address of the ISAUS Commissioner of Patents and Tradetrana's Box PCT Washington, D.C. 20231		on searched other than minimum documentation to the	extent that such docu	ments are included	in the fields searched		
Category*  Citation of document, with indication, where appropriate, of the relevant passages  Relevant to claim No.  US 5,352,493 A (DORFMAN et al) 04 October 1994, col. 6. lines 1-10.  Y  US 5,466,431 A (DORFMAN et al) 14 November 1995, col. 3, lines 50-68.  Y,P  US 5,786,068 A (DORFMAN et al) 28 July 1998, col. 5, lines 35- 60.  **Special categories of cited documents: **A' **Special categories of cited documents to be oparticular relevance **By earlier document published on or after the international filing date to be oparticular relevance **Second content of particular relevance, the chained invention cannot be special reason (as pacifical) **Commission principly date chained invention cannot be document referring to an oral disclosure, use, exhibition or other the principle relevance, the chained invention cannot be document referring to an oral disclosure, use, exhibition or other the principle relevance, the chained invention cannot be document referring to an oral disclosure, use, exhibition or other the principle relevance, the chained invention cannot be document referring to an oral disclosure, use, exhibition or other the principle relevance, the chained invention cannot be document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other the principle relevance, the chained invention cannot be document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use, exhibition or other document referring to an oral disclosure, use,		ata base consulted during the international search (nat	me of data base and	, where practicable,	search terms used)		
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Innex 50-68.   Y,P	Y		4 October 1994	, col. 6. lines	1-30		
Further documents are listed in the continuation of Box C.  See patent family annex.  Special estegories of cited documents:  'A' document defining the general state of the art which is not considered to be of particular relevance document under the principle and to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(d) or which is cited to establish the publication date of another citation or other special reason (as specified)  'C' document referring to an oral disclosure, use, exhibition or other means  'P' document published prior to the international filing date but later than the priority date claimed  Date of the actual completion of the international scarch  22 JUNE 1999  Name and mailing address of the ISA/US Commissioner of Patients and Trademarks  Box PCT Washington, D.C. 20231	Y	09 5,400,451 11 (Bold Mill) of all 11 11010 most 1770,					
Special categories of cited documents:  "A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier document published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the priority date claimed  Date of the actual completion of the international search  22 JUNE 1999  Name and mailing address of the ISA/US Commissioner of Patents and Trademarks  Box PCT  Washington, D.C. 20231  Ister document published after the international filing date or priority date and not in conflict with the specieston but cited to understand the principle or theory underlying the invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "X"  document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  "A"  document member of the same patent family  Date of mailing of the international search report  02 JUL 1999  Authorized officer  RICHARD K. LEE	Y,P		8 July 1998, co	I. 5, lines 35-	1-30		
*A* document defining the general state of the art which is not considered to be of particular relevance  *E* earlier document published on or after the international filing date  *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  *O* document referring to an oral disclosure, use, exhibition or other means  *P* document published prior to the international filing date but later than the priority date claimed  Date of the actual completion of the international search  22 JUNE 1999  Name and mailing address of the ISA/US Commissioner of Patents and Trademarks  Box PCT  Washington, D.C. 20231  document of particular relevance; the claimed invention cannot be considered novel or cannot be considered no involve an inventive step when the document is taken alone  ***  ***  ***  ***  **  **  **  **	Furti	her documents are listed in the continuation of Box C	. See pat	ent family annex.			
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